

SYMPOSIUM ON CHARACTERIZATION AND CHEMISTRY OF OIL SHALES
PRESENTED BEFORE THE DIVISIONS OF FUEL CHEMISTRY AND
PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
ST. LOUIS MEETING, APRIL 8 - 13, 1984

RAPID HEAT-UP ASSAY FOR EASTERN OIL SHALES

By

C. A. Audeh

Mobil Research and Development Corporation, Central Research Division, P. O. Box 1025
Princeton, New Jersey 08540

INTRODUCTION

Interest in the exploitation of eastern oil shales is related to the economics of their location. Advantages such as the availability of the needed water resources and a labor pool with experience in mining as well as processing are usually cited in favor of the future development of these shales. Also, the proximity of the markets of the east coast to the resource makes their development attractive. However, eastern shales, in general, give low oil yields in the Fischer Assay. Since the Fischer Assay has been considered as a means of predicting oil yield from commercial processing of oil shale (1), the exploitation of eastern shales based on this yield evaluation becomes doubtful.

Many eastern shale deposits have been analyzed (2, 3) and assessed as to their commercial prospects (2) on the basis of their oil yield, carbon content and thickness. In general, eastern shales can be matched with samples from western shales with the same carbon content. However, the Fischer Assay yield of oil from a western shale exceeds that from an eastern shale with the same carbon content. For example, whereas a western shale with 13.6 wt % organic carbon yields 11.4 wt % oil (about 30 gallons per ton, g/t) an eastern shale with 13.7 wt % organic carbon yields 4.6 wt % oil (about 12 g/t) (4). These yields correspond to 73% and 30% conversion of organic carbon to oil.

Several reports (5-7) have suggested that oil yields from eastern shales are influenced by the rate at which the retorting temperature is reached. Thus, it was reported that when the rate of heat-up was increased to 55°C/min, vs. 12°C/min for the Fischer Assay (8), an oil yield 125% of Fischer Assay was obtained (5). Further, at much higher heat-up rates, 6,000°C/min (7) and 33,000°C/min (6), an increase of up to 140% of Fischer Assay oil yield was calculated. These calculated yields, however, were estimates based on the residual carbon content of the shale after retorting under Fischer Assay conditions and upon retorting in a fluidized bed unit (6). Yields were also calculated by measurement of relative areas under a chromatogram and elemental analyses of the spent shales (7). Although yields of shale oil were determined (5) or estimated (6, 7), oil characterization was not reported.

Clearly, there is no standard retorting procedure comparable to the Fischer Assay that is applicable to eastern shales wherein rapid heat-up (RHU) to the desired pyrolysis temperature could be used for determining the potential oil yield of an oil shale. Oil yield and oil properties are two essential characteristics needed for economic assessment of a shale resource. Thus, the development of a rapid heat-up assay for eastern shales that can generate collectible quantities of oil that could be characterized is necessary. Such an assay has been developed and it is proposed that it be adopted as a common procedure for determining the oil yield from shales under rapid heat-up conditions.

EXPERIMENTAL

Retort

Figure 1 depicts the rapid heat-up retort used in these experiments. The retort was constructed from two 6" x 6" stainless steel plates, 1/8" thick and a standard bolted flat flange. A 1/4" spacer was used along three edges of the plates to create a 6" x 6" x 1/4" "pocket" with a capacity of at least 100 gm. At the bottom of the pocket reactor (PR), a sweep gas inlet was connected to a diffuser through a plenum. The PR was sealed by bolting the loose top flange to the flange attached to the body of the retort. A high temperature gasket was placed between the two flanges to prevent product leakage. Two thermocouples, placed halfway in the bed of shale, were used to observe the temperature in the retort. The temperature was continuously monitored and recorded on a strip chart recorder. Products were allowed to leave the PR through an outlet connected to

the recovery system by a glass ball joint.

Retort Heater

A fluidized sand bath was used in all experiments. The sand bath temperature was set to about 575°C and maintained at that temperature.

Oil Recovery System

The system described in the Fischer Assay (8) was modified by using a -10°C bath for the centrifuge tube and by circulating -10°C coolant in an efficient glass condenser. However, other arrangements could be used to achieve the desired recovery of oil, as for example those described in (1, 5 and 9).

Gas Measurement

H₂S was removed as cadmium sulfide and the non-condensable gas was measured by means of a wet test meter.

Retorting Procedure

The loaded PR was connected to the inert gas lines and the flow adjusted to 10-15 ml/min. When the desired sand bath temperature (575°C) was reached, the PR was dropped into the bath and the product outlet immediately connected to the recovery system. As the inside temperature of the PR approached 480-485°C, the temperature of the sand bath was allowed to cool to about 515°C so that the retort temperature did not exceed 500-505°C. This temperature was then maintained for 30 minutes.

Oil Shale Samples

The various samples of oil shale used were collected from Bullitt County, Kentucky. Each sample was crushed and sieved. Particles, 16/28 and 28/35 mesh were collected. In some cases, a 16/35 mesh fraction was collected. All crushed samples were stored under argon.

RESULTS AND DISCUSSION

Retort Heat-Up Profiles

In a Fischer Assay, it is generally stated (1, 5-7) that the heat-up rate is 12°C/min. However, in the required heat-up profile (8), six distinct and different heat-up rates can be identified. These are:

- | | | | |
|----|-----------|------------------------|----------|
| 1. | 0-10 min | the rate is < 1°C/min | to 30°C |
| 2. | 10-20 min | the rate is 20°C/min | to 225°C |
| 3. | 20-30 min | the rate is 12.5°C/min | to 350°C |
| 4. | 30-36 min | the rate is 10°C/min | to 410°C |
| 5. | 36-44 min | the rate is 8°C/min | to 475°C |
| 6. | 44-55 min | the rate is 4°C/min | to 500°C |

Also, this profile corresponds to the temperature of the base of the Fischer retort and not the shale in the retort. By modifying the Fischer retort to allow for the measurement of its internal temperature, it was determined that there is a difference of about 70°C between the shale nearest the wall of the retort and its center. Even shale < 1/4" from the retort wall is 17°C cooler than the base.

For the RHU assay described, the actual temperature of the shale was measured and in the resultant profile, three distinct and different heat-up rates were identified. These were:

- | | | | |
|----|-------------|------------------------|----------|
| 1. | 0-2.5 min | the rate was 114°C/min | to 310°C |
| 2. | 2.5-5.0 min | the rate was 56°C/min | to 450°C |
| 3. | 5-7.5 min | the rate was 20°C/min | to 498°C |

However, since the bed of shale in the RHU retort is 1/4" in thickness, no temperature gradient was detectable across the 6" x 6" x 1/4" retort. It is estimated that the 1/4" bed is made up of about 10 shale particles and, since heat was uniformly applied from all directions, the heat-up profile of each 1/8" of shale is also uniform. Thus, overall, it was concluded that all the shale was retorted at the same temperature.

In control experiments, it was observed that two effects influence the observed decrease in heat-up rate: First, Δt , the difference between the temperature of the sand bath and the bed temperature of the retort. Second, the formation of oil during retorting. As the internal temperature increases and Δt becomes small, heat transfer is reduced and as oil is formed, the demand for energy increases. Both effects work in the direction of reducing the heat-up rate. It was not possible to study these effects separately; however, it was observed that when oil formation started the heat-up rate always decreased.

Oil formation was accompanied by the formation of gas. Also, about 90% of the oil produced was recovered during the 375-475°C temperature interval, which corresponds to a period of

about 2 minutes. This is in contrast with the Fischer Assay in which the same temperature interval corresponds to about 12 minutes during which less than 50% of the oil is collected. As pointed out earlier, the temperature of the shale in a Fischer retort does not correspond to that of the base of the retort and there exists within the retort a significant temperature gradient. Thus, whereas oil generation in the RHU retort proceeds uniformly and at the same temperature throughout the bed, in the Fischer retort, it proceeds across steep temperature gradients in time and space.

Yield of Products

Rapid heat-up to retorting temperatures results in a higher oil yield than that obtained in the Fischer Assay, Table I. All the eastern shales tested gave from about 150% to 200% of Fischer Assay. This observation is consistent with predicted increases for eastern shales and is achieved at lower heat-up rates than the 6,000-30,000°C calculated (6, 7). It also confirms the directional increase based on experiments carried out at a heat-up rate of about 50°C/min.

TABLE I

YIELDS OF OIL FROM FISCHER ASSAY AND RAPID HEAT-UP ASSAY OF OIL SHALES

Sample	Fischer Assay Gallons/Ton	Rapid Heat-Up Gallons/Ton
Kentucky, Bullitt Co.		
1 B	9.4	17.4
1 C	8.7	17.9
1 D	9.3	18.4
1 E	11.5	21.3
Drum	10.8	16.2

The other yields determined, Table II, were those of the gas that did not condense in the product recovery system, H₂S and retort water. It was observed that the volume of gas generated in RHU retorting was greater than that generated in the Fischer Assay. In contrast, the amount of water collected was the same and that of hydrogen sulfide smaller.

TABLE II

YIELD OF OIL, GAS AND H₂S FROM FISCHER ASSAY (FA)^a AND RAPID HEAT-UP ASSAY (RHUA)^b

Sample I. D.	Oil, % Wt		Oil G/T		Gas 1/100g		H ₂ S, % Wt	
	FA	RHUA	FA	RHUA	FA	RHUA	FA	RHUA
1B	3.5	6.9	9.4	17.4	1.41	ND*	0.9	0.7
1C	3.2	7.1	8.7	17.9	1.61	2.03	1.9	1.6
1D	3.5	7.3	9.3	18.4	1.74	2.03	1.2	0.8
1E	4.4	8.5	11.5	21.3	1.82	2.68	1.5	1.2
Drum	4.3	6.3	11.3 ^c	16.0 ^d	1.20	1.60	1.1	0.9

a. Heat-up to 500°C at - 12°C/min, 1/2 hr at 500°C.

b. Heat-up to 500°C at an initial rate of about 100°C/min, 1/2 hr at 500°C.

c. Average of 3 determinations; 11.8, 10.8 and 11.4 G/T.

d. Average of 3 determinations; 15.8, 15.8 and 16.3 G/T.

* ND - Not determined.

H₂S formation during retorting has been studied previously for western shale (10). However, little or no information is available for eastern shales (11). In all the experiments carried out, significant amounts of H₂S equivalent to about 1% S by wt of the sample retorted were formed. The source of H₂S is organically combined sulfur and pyrite (10). Both types of S are present in the shale. The kerogen contains the organic sulfur, which upon retorting, is converted to product oil and H₂S. Pyrite, on the other hand, does not form H₂S in the absence of a hydrogen source. During retorting several hydrogen sources are available for the pyrite/H reactions. Kerogen, oil-forming intermediates, hydrocarbons in the product oil as well as the oil's various heteroatomic species and steam are likely H-sources.

In separate experiments, the dependence of the formation of H_2S from pyrite on a source of hydrogen was confirmed. By treating a spent shale, obtained as a result of a Fischer Assay, with steam, significant amounts of H_2S were generated. H_2S was also formed in significant amounts when a sulfur-free crude oil fraction was retorted in the presence of pyrite-containing spent shale.

During the retorting of an eastern shale the appropriate environment exists for the reaction of pyrite with a hydrogen source. Also in the Fischer Assay the time the hydrogen source could be in contact with the pyrite is 10 times as long as that in the RHU assay. This difference could be the reason for the lower yield of H_2S generated by RHU than that generated in the Fischer Assay.

Product Properties

Gas - Increasing the heat-up rate during retorting generates a larger volume of gas/100 gms of oil shale than that generated in a Fischer Assay. This increase in gas yield was not the same for all the shales studied. For example, one eastern shale sample tested generated about 15% more gas, another generated 50% more. The increases in gas yield, however, were accompanied by increases of 100% and 85% in the Fischer Assay yield, respectively. It is possible that some correlation could be established between gas yield in the RHU assay and that of the Fischer, however, the data available so far are not sufficient for this purpose.

The composition of RHU gas shows little variation for different shale samples. Also, the differences in concentration between the main components of RHU and the Fischer Assay gases are minimal, Table III. An interpretation of this observation is consistent with the thermal treatment of the shale in the two assay procedures. Since, in both assays, the maximum temperature to which the oil shale and the product oil are exposed is the same, the extent of thermal cracking to lighter fragments would be similar. This observation is consistent with that made for delayed coking of petroleum residual oil wherein it is higher temperatures, not longer times, that result in secondary cracking of product oil and produce a change in the composition of the gas generated (12).

TABLE III

YIELD AND COMPOSITION OF GAS FROM FISCHER AND RHU RETORTING OF
A BULLITT COUNTY, KENTUCKY, OIL SHALE (SAMPLE 1D)

<u>Retort</u>	<u>Fischer</u>	<u>PR</u>
Heat-up rate, °C/min	12	100 ^a
Gas, liters/100gm, H_2S free	1.74	2.03
H_2S , % Wt	1.2	0.8
Gas Analysis, Mol %		
H_2	40.6	39.6
CH_4	27.0	26.4
C_2H_4	2.1	2.2
C_2H_6	3.1	2.1
C_3H_6	3.1	2.1
C_3H_8	2.9	2.7
C_4H_8	1.6	0.5
C_4H_{10}	1.7	0.9
CO	2.6	4.0
CO_2	9.0	12.0
Gas + H_2S , l/100 g	2.53	2.56
% H_2S	31	21
% Gas	69	79

a. Initial heat-up rate.

Oil - As with the Fischer Assay, the amounts of oil generated in the RHU assay vary with the oil shale used. Also, because of the batch nature of both assays and the size of sample, 100 gms., these amounts of oil are necessarily small. Thus, the extent to which the assay oils can be tested is limited. For these experiments, the same tests were carried out on oils produced from both assays. In Table IV, data are present for product oils obtained for one eastern shale. The differences in properties are typical and the data shown for oils obtained from the two assay procedures are consistent with data obtained for other eastern shale samples.

TABLE IV
COMPARISON OF PROPERTIES OF SHALE OIL OBTAINED FROM FISCHER AND
RHU RETORTING OF A BULLITT, COUNTY, KENTUCKY OIL SHALE (DRUM SAMPLE)

<u>Retort</u>	<u>Fischer</u>	<u>RHU</u>
Heat-up rate, °C/min	12	100 ^a
Oil yield G/T	10.8	16.2
% Wt	4.3	6.3
Spent shale, % wt	92	88
Gas yield, liters/100 gm	1.2	1.6
H ₂ S yield, % wt	1.1	0.9
Water, % wt	1.5	1.7
<u>Oil Properties</u>		
Gravity, °API	26.1	21.6
Specific gravity, 60°F/60°F	0.8978	0.9242
Pour point, °F	-50	-40
Aromatic carbon, %	40	41
<u>Elemental Analysis, wt %</u>		
C	84.42	84.59
H	11.09	10.52
N	1.35	1.14
S	1.81	1.64
<u>Distillation, ASTM D2887, %</u>		
C ₅ - 400°F	24	22
400 - 550	18	13
550 - 710	27	19
710 - 1000	30	45
1000°+	< 1	1
<u>Shale, Spent and (Fresh)</u>		
<u>Elemental Analysis, % Wt</u>		
C (Fresh)	8.88 (12.60)	7.39
H	0.55 (1.32)	0.34
N	0.33 (0.38)	0.36
S	5.86 (6.58)	5.50
Ash, % wt	88.3 ----	86.6
Pyritic sulfur	---- (6.42)	----

a. Initial heat-up rate.

A salient and consistent observation is the difference in the gravity between oil collected from the Fischer Assay and that from the RHU assay. Invariably, a difference in gravity of about 4-5° API is observed. RHU oils are denser, i. e., have the lower API gravity. This reduction in API gravity is consistent with the idea that oil precursors are thermally converted to oil products with a wide range of molecular weight. Since, in the RHU assay, the time taken to reach retorting temperatures is short and a stripping gas is used, the heavier components are removed from the retort rapidly and are condensed in the oil with the lighter components. In the Fischer Assay, these conditions do not prevail. Some of the heavier components partially condense and remain with the shale or are further cracked to form the lighter products. Another observation supports this interpretation. The boiling point distribution of RHU assay oil shows larger amounts of the 700°F⁺ distillate than that of the Fischer Assay product. In both assays, however, the distillate contains little or no 1000°F⁺ residue, reflecting the - 930°F maximum retorting temperature of both tests.

Another difference between the oils is in the hydrogen to carbon ratio. RHU assay oil H/C ratio again reflects the heavier nature of the product oil. Whereas Fischer Assay oil typically has

RAPID HEAT-UP RETORT

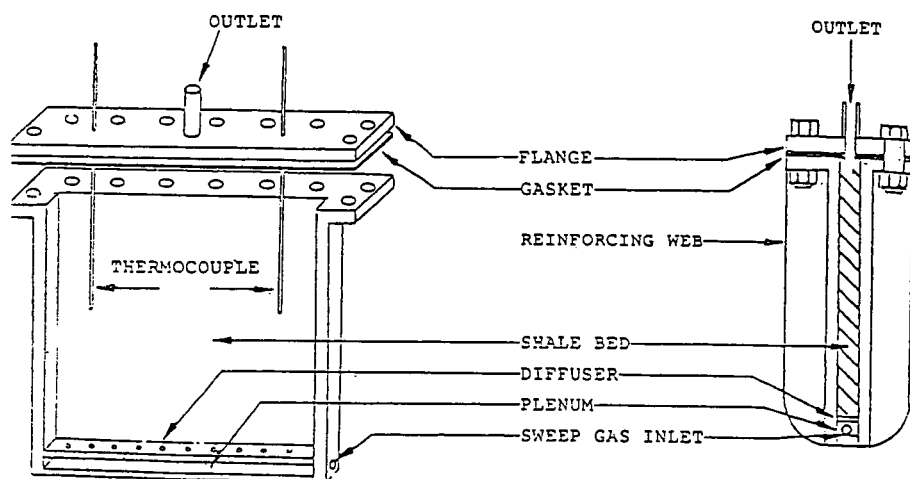


Figure 1

10.5-11% wt hydrogen, that of RHU assay is about 1% lower for the same carbon content. This observation is consistent with the boiling range shift towards heavier distillates and is in agreement with the qualitative assessment described as a chromatographically "unresolved hump in the C₂₀-C₃₀ range" obtained from fluidized bed pyrolysis of eastern oil shale (13). It is also supported by studies of Kuckersite shales in fixed bed retorting (14).

Sulfur and nitrogen concentrations in the RHU assay oils are similar to those of the Fischer Assay oils. The available data point towards a dependence of S and N content of the oil on the S and N concentration of the raw shale. However, these data are not sufficient for developing a correlation that would predict the sulfur and nitrogen concentrations of the product oil. As mentioned earlier, pyrite is a common component of eastern shales and this has to be taken into consideration when developing the sulfur correlation.

The pour points of the eastern shale oils produced were below -40°F. Little or no dependence on retorting method was observed for this property.

Carbon type distribution, aromatic and aliphatic, in the oils produced by the two assays was the same. Oil from the Fischer Assay had 40% aromatic carbon and that from the RHU assay 41%. Considering the accuracy of the nmr determination this result shows that RHU retorting of a shale does not change this characteristic of the product oil. Although a boiling point shift towards heavier products was observed, this change was either averaged over both types of carbon or were too small for detection by ¹³C nmr.

Spent Shale

Elemental analyses of spent shale produced by RHU retorting confirmed the increased conversion of kerogen carbon to product oil. Both carbon and hydrogen in the spent shale reflected the improvement in the conversion of kerogen to products. However, duplicate results for some samples were inconsistent. Particularly troublesome were hydrogen determinations on the spent shales. Directionally, however, the reduced hydrogen content of spent shale from RHU and Fischer Assays was correct.

CONCLUSIONS

A rapid heat-up assay for eastern shales that can generate collectible quantities of oil that can be characterized has been developed. It is proposed that it be adopted as a common procedure for determining the oil yield of an eastern shale.

LITERATURE CITED

- (1) Goodfellow, L. and Atwood, M. T., Proc. 7th Oil Shale Symp. Quart CSM, 69, 205 (1974).
- (2) Janka, J. C. and Dennison, J. M., Symp. papers: Synthetic Fuels from Oil Shale, Atlanta, GA, p. 21 (1979).
- (3) Smith, J. W. and Young, N. B., Chem. Geology, 2, 157 (1967).
- (4) Miknis, F. P. and Maciel, G. E., Proc. 14th Oil Shale Symp., p. 270 (1981).
- (5) Rubel, A. M. and Coburn, T. T., Proc. 1981 Eastern Oil Shale Symp., p. 151 (1981).
- (6) Margolis, M. J., Ibid., p. 151.
- (7) Reasoner, J. W., Sturgeon, L., Naples, K. and Margolis, M. J., Ibid., p. 11.
- (8) ASTM D 3904-80.
- (9) Wallman, P. H., Tam, P. W. and Spars, B. G., ACS Symp. Series No. 163, Paper No. 7, p. 93.
- (10) Burnham, A. K., Kirman Bey, N. and Koskinas, G. J., Ibid., paper No. 5, p. 61.
- (11) Rostam-Abadi, M. and Mickelson, R. W., 91st Natl. Meeting AIChE, Detroit, Paper 16B, (1981).
- (12) Audeh, C. A. and Yan, T. Y., ACS Symp. Series 202, Coke Formation on Metal Surfaces, ACS, Washington, D.C. (1982).
- (13) Burnham, A. K., Richardson, J. H. and Coburn, T. T., UCRL-87587, Preprint (1982).
- (14) Urove, K. E., Khimiya Tverdogo Roplica, 10, No. 5, 33 (1976).